HML METHOD 939-M

Method Status: Operational

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Determination of Organic Lead Compounds by Graphite Furnace Atomic Absorption Spectrometry

1. Scope and Application

1.1 This method is used to determine the sum of organic lead compounds ("organolead") in liquids (aqueous, organic solvents, waste water etc.) solids or sludge.

1.2 The method is based on: a) "Standard Test Method for Lead in gasoline by Atomic Absorption Spectrometry" by American National Standard Institute/American Society for Testing and Materials (ANSI/ASTM), ASTM D3237-79. b) A procedure originally developed in the Du Pont Petroleum Laboratory for the determination of organic lead in leaded gasoline tank sludge. (See References, subdivision 12.1)

2. Summary of Method

2.1 Organolead is separated from the sample matrix by extraction with p-xylene. The organolead in the extract is reacted with Aliquat 336 and iodine and the solution is made up to volume with p-xylene. Lead contained in this mixture is determined by graphite furnace atomic absorption spectrometry.

3. Safety

3.1 Some organic lead compounds are volatile and toxic. Therefore, samples must be processed in a well ventilated hood. Antiknock lead compounds are particularly poisonous and must not be inhaled or ingested or allowed to come into contact with the skin. Antiknock lead compounds should never be exposed to elevated temperatures (above 50 EC) or to acids and oxidizing agents. Whenever organic lead compounds are handled outside of a well ventilated-hood, protective respiratory equipment, protective clothing and rubber gloves must be worn. The material safety data sheets (MSDS) for organolead standards must be read.

3.2 The solvents and samples used in this method are flammable. Proper precautions must be taken to prevent contact with sparks or open flames.

3.3 Hazardous ultraviolet radiation can be emitted by the atomizer, hollow cathode lamps, and electrodeless discharge lamps. This radiation can cause serious damage to human eyes. Always wear safety glasses which are certified or warranted to protect the eyes from ultraviolet radiation.

3.4 When the graphite tube atomizer is operating, the magnet, atomizer chimney, and immediate surrounds can present heat hazards which can result in burns. Never touch the magnet, atomizer chimney, or the atomizer assembly while the graphite tube atomizer is operating. Wear protective gloves when working near the magnet.

3.5 The magnet produces a variable magnetic field of 8000 gauss RMS at mains frequency in the workhead during the read stage. To avoid interference with heart pacemakers or magnetic storage media, keep them at least 300 mm from the magnet.

3.6 The graphite tube atomizer gas supply system is designed for use with inert gases and air. The system is not designed for use with pure hydrogen. Never use pure hydrogen with the graphite tube atomizer since this could result in leakage and potentially explosive accumulation of hydrogen. However prepackaged mixture of 95% argon and 5% hydrogen can be used. Never create your own mixture of hydrogen and an inert gas through the GTA system.

4. Interferences

4.1 To reduce loss of organic lead compounds which are volatile and sensitive to oxygen, samples must not be exposed to elevated temperatures or to air for extended periods of time. Such losses are minimized by adhering to the sample collection, preservation, and handling procedures in sections 7.2-7.4 and 8.1.1.

4.2 If the samples are moist, there may be poor wettability with xylene. Use anhydrous sodium sulfate to dry the sample.

4.3 A 0.1% H_3PO_4 solution must be added to all extracts prior to analysis to permit the use of a higher ashing temperature and stabilization of the Pb signal.

4.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected by means of black burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

5. Apparatus and Materials

5.1 Atomic absorption spectrophotometer, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, background corrector, and recorder or integrator.

5.2 Lead hollow cathode lamp or electrodeless discharge lamp.

5.3 Graphite furnace with the appropriate temperature and timing controls.

5.4 A chart recorder or integrator is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

5.5 Erlenmeyer flasks, 250 mL, and 100 mL with ground glass stoppers

5.6 Ambient temperature mechanical shaker (oscillation rate of ~ 60 per minute) or equivalent.

5.7 Glass filter funnel and filter paper (Whatman #40, #42 or equivalent).

5.8 Separatory funnels, > 250 mL capacity.

5.9 Volumetric flasks, 1000 mL, 250 mL, 100 mL and 50 mL

5.10 All glassware should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and deionized water.

6. Reagents

All solvents and reagents must be at least analytical reagent grade, if available.

6.1 p-xylene, assay (GC) 98% minimum.

6.2 Methyl alcohol GR, A.C.S.

6.3 Iodine: Reagent Grade, A.C.S. Iodine solution: Dissolve 3.0 g of elemental iodine in xylene and make up to 100 mL with the same solvent. Store in a brown bottle in a refrigerator.

6.4 Aliquat 336 (Tri-capryl methyl ammonium chloride), available from Aldrich, Milwaukee, WI, or from McKesson Co., Minneapolis, MN. Aliquat is a registered trademark of Henkel Corporation.
Prepare two solutions, one containing 10 % (w/v) and one containing 1 % (w/v) in xylene. Store in a refrigerator.

6.5 Anhydrous sodium sulfate, granular, Reagent Grade.

6.6 Lead chloride, crystals, Reagent Grade; dry at 105 ^{o}C for 3 hours before use.

6.6.1 Prepare a stock solution containing 1000 mg/L of Pb by dissolving 0.3356 g of lead chloride in 10 % Aliquat 336 in xylene and dilute to 250 mL. Store in a brown bottle in a refrigerator.

6.6.2 Prepare a primary intermediate Pb standard 20 mg/L by pipetting 2.0 mL of the stock standard into a volumetric flask and diluting to 100 mL with xylene. Store in a brown bottle in a refrigerator.

6.7 Reference Standard, NIST, SRM 2715 (Lead in Reference fuel)

6.8 Sodium Chloride, GR, A.C.S.

6.9 Orthophosphoric Acid, Reagent Grade, A.C.S.

6.10 Triton X-100

6.11 HNO_3, Reagent Grade, A.C.S.

7. Sample Collection, Preservation, and Handling

7.1 For safety precautions see section 3.0.

7.2 Liquid samples must be collected in amber glass bottles (preferably 1 pint) with Teflon-lined caps without leaving any headspace. During sampling, contact of the sample with air must be minimized.

7.3 Solid samples must be collected in 4 oz. amber glass jars with airtight, Teflon-lined lids (fill to minimize headspace).

7.4 All samples must be transported and stored at refrigerator temperature (approximately 4 EC).

8. Procedure

The order of addition of the reagents must be followed explicitly. Aliquat 336 must not be added before the addition of iodine because it retards the formation of the alkyl lead iodide-Aliquat 336 complex, giving erroneous results.

8.1 Extraction of Solid and Sludge Samples

8.1.1 Weigh out (to the nearest 0.1 g) about 50 g of homogenized sample into an Erlenmeyer flask, if the sample is moist or wet, add 10 g (or more depending on the moisture content of the sample) of anhydrous sodium sulfate, make a homogenous mixture. Add 100 mL of p-xylene in three portions of 50.0, 25.0 and 25.0 mL each.

Stirring of the sample with a mechanical or magnetic stirrer must not be substituted for shaking since it can result in loss of organolead due to oxidation by air oxygen. For the same reason, extraction times of more than 30 min must be avoided.

8.1.2 Extract first with 50.0 mL of p-xylene. Stopper the flask and shake on a mechanical shaker for 15 min. Decant the p-xylene extract into a 100 mL flask with ground glass stopper.

8.1.3 Add the second portion of 25.0 mL of fresh p-xylene to the same sample. Extract again for five minutes. Decant the extracted p-xylene to the first extract.

8.1.4 Repeat step 8.1.3 with another 25.0 mL of p-xylene.

8.1.5 Prior to filtration, thoroughly rinse the filter paper containing 10 g of anhydrous sodium sulfate using p-xylene.

8.1.6 Filter the combined extract into a flask through the filter paper holding about 10 g of rinsed anhydrous sodium sulfate .

8.1.7 Pipet 40 mL of the filtered sample into a 50 mL volumetric flask.

8.1.8 To the same flask, add 0.1 mL of iodine solution and mix gently. Let it react for approximately 1.0 min.

8.1.9 To the same flask, add 5 mL of 1 % Aliquat 336 in p-xylene, dilute to volume with p-xylene and mix. Analyze by GFAAS.

8.2 Extraction of Liquid Samples

8.2.1 (p-Xylene Soluble)

8.2.1.1 Place 10 mL aliquot of sample and 10 mL of p-xylene into a flask, stopper it and shake for few minutes. If a single liquid phase is obtained, i.e., if the sample is completely soluble in p-xylene, discard the sample/p-xylene mixture.

8.2.1.2 Pipet 20 mL of sample into a 100 mL volumetric flask. Make it to volume with p-xylene and mix well.

8.2.1.3 Prior to filtration, thoroughly rinse the filter paper containing 10 g of anhydrous sodium sulfate using p-xylene.

8.2.1.4 Filter the sample solution (8.2.1.2) into a flask through the filter paper holding about 10 g of rinsed anhydrous sodium sulfate .

8.2.1.5 Continue as described in steps 8.1.7 - 8.1.9.

8.2.2 (p-Xylene Insoluble)

8.2.2.1 Place 200 mL of the well mixed sample and 50 mL of p-xylene into a separatory funnel and shake for 2 min. Allow 5-10 min for phase separation.

8.2.2.2 If an emulsion is obtained which requires more time for phase separation, add about 5 g of NaCl to the separatory funnel, shake briefly, and let the mixture settle for 20 min.

8.2.2.3 After separation of the p-xylene layer from the sample (e.g., water), drain off the sample into a beaker and collect the p-xylene extract in a 100 mL flask with ground glass stopper. Pour back the sample from the beaker into the separatory funnel.

8.2.2.4 Add 25 mL of fresh p-xylene to the beaker, rinse the beaker well, add to sample, shake for 2 min and allow 5 -10 min for phase separation.

8.2.2.5 Repeat step 8.2.2.3, adding the p-xylene phase to the first extract. Then repeat steps 8.2.2.4 and 8.2.2.3 with another 25 mL of p-xylene.

8.2.2.6 Prior to filtration, thoroughly rinse the filter paper containing about 10 g of anhydrous sodium sulfate using p-xylene.

8.2.2.7 Filter the combined extract into a flask through the filter paper holding about 10 g of rinsed anhydrous sodium sulfate.

8.2.2.8 Pipet 40 mL of the filtered extract into a 50 mL volumetric flask and mix. Continue as described in step 8.1.8 and 8.1.9.

8.3 Standard and Blank Preparation

Prepare a secondary intermediate Pb standard 500 ug/L by pipetting 2.5 mL of the primary intermediate Pb standard (6.6.2) into a volumetric flask and diluting to 100 mL with p-xylene.

Note: The above standard solution prepared from lead chloride should not be used for spiking the sample solution. Leaded gasoline or Reference Standard with a known concentration of organolead must be used for spiking.

8.3.1 Place 40 mL of p-xylene into a 100 mL volumetric flask and add the correct amount of the 500 :g/L standard to prepare the desired concentration.

8.3.2 Immediately add 0.2 mL of iodine solution and mix well.

8.3.3 Add 10 mL of 1 % Aliquat 336 solution, dilute to volume with p-xylene and mix well.

8.3.4 The blank is prepared in the same way as the calibration standards (steps 8.3.1 - 8.3.3), except that no organolead intermediate standard is added.

8.4 Chemical Modifier Preparation: (0.1% H_3PO_4)

Prepare a chemical modifier by pipetting 2.0 mL of Orthophosphoric acid in Methanol into a one liter volumetric flask.

8.5 Rinse Solution Preparation: Triton X-100 0.01% v/v & HNO_3 0.1% v/v
If an autosampler is used, prepare the rinse solution by adding a drop of Triton X-100 and 1.0 mL of nitric acid into a liter volumetric flask containing ~100 mL of deionized water. Dilute to volume with deionized water and mix well.

8.6 Graphite Furnace Atomic Absorption Measurements

Since certain organolead compounds are volatile, heat, vapors and fumes generated by furnace methods can be hazardous and toxic. Heat, vapors and fumes must be extracted from the instrument by means of the exhaust system.

8.6.1 The GFAAS spectrometer is set up according to the manufacturers instructions.

8.6.2 Measure the absorbance of the method blank, working standards, and samples.

8.6.3.1 If sample readings fall outside the calibrated range, the solutions must be diluted with p-xylene again.

8.6.4 The following Instrument parameters and Furnace operating conditions are for Varian Zeeman GTA, Spectra AA-300 using a notched partitioned graphite tube & forked pyrolytic platform. (For other manufacturers follow the manufacturer's suggestions for spectrophotometer and furnace parameters, there will be some variations from one manufacturer to the other.)

Wavelength (nm)	283.3
Calib.mode used	Conc.
Meas.mode used	Peak Area
Lamp current (ma)	5
Slit width (nm)	0.5
Slit height	Reduced
Backgrd. corr	ON
Hot Inject	YES
Temperature ^{o}C	80
Inject Rate	3
Modifier used	0.1% H_3PO_4 in Methanol
Dry stage temp ^{o}C &Time(sec)	95, 150, 180 & 20, 10, 25
Ash stage temp ^{o}C &Time(sec)	500, 700, 850 & 15, 10, 20
Atomize temp ^{o}C & Time (sec)	2500, 2500 & 1.2, 2.0
Sample vol.(:L)	20
Modifier vol. (:L)	5

8.6.5 Run a check standard after every ten samples; check standard should be from a different source than calib. standards. Check standard concentration level should be at

or near the middle of the calibration range. The standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

9. Calculations

Depending on the type of sample analyzed and the method of sample preparation, one of the following three formulas is used to calculate the concentration of organolead in the sample:

9.1 Solid and Sludge Samples

$$\text{Conc (:g/Kg)} = \text{GFAA-Result (:g/L)} \times \frac{100\ \text{mL}}{W\ (g)} \times \frac{50\ \text{mL}}{40\ \text{mL}}$$

where W (g) is the sample mass in grams (usually 50 g).

9.2 Liquid Samples soluble in p-xylene

$$\text{Conc (:g/L)} = \text{GFAA-Result (:g/L)} \times \frac{100\text{mL}}{V(\text{mL})} \times \frac{50\text{mL}}{40\ \text{mL}}$$

where V(mL) is the sample volume in mL (usually 20 mL).

9.3 Liquid Samples not soluble in p-xylene

$$\text{Conc (:g/L)} = \text{GFAA-Result (:g/L)} \times \frac{100\ \text{mL}}{V(\text{mL})} \times \frac{50\ \text{mL}}{40\ \text{mL}}$$

Where V(mL)is the sample volume in mL(usually 200 mL).

10. Quality Control

10.1 Prepare a calibration curve each day with a reagent blank and a minimum of three working standards ranging from 5.00 - 50.0 ug/L using secondary intermediate Pb standard (8.2). After calibration, verify the calibration curve by use of a blank and a calibration check standard (prepared from a reference material or other independent standard material) at or near the mid-range. The working calibration range must

conform to QC requirements of less than 20% RSD or greater than or equal to 0.995 correlation coefficient. The calibration check standard must be within 10 % of it's true value for the curve to be considered valid.

10.2 Analyze a method blank along with each batch of ten samples (or less). If the blank indicates a significant contamination (more than twice the method detection limit), repeat the procedure with samples and blank.

10.3 If more than 10 samples per day are analyzed, the calibration curve must be verified by measuring a mid-range reference standard after every 10 samples. The value of this standard must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

10.4 Analyze a duplicate sample with each batch of ten samples or fewer. If sample does not contain the analyte (organolead), confirm by analyzing a matrix spike / method of standard additions.

10.5 Analyze a matrix spiked sample with each batch of ten samples or less. The level of spiking must be about twenty times the instrument detection limit. If the sample contains measurable organic lead, the spike level must be at least two to four times the measured level. This matrix spike should be added to sample solution before extraction.

10.6 Post Extract QC- a post extract spike at 10 to 20 :g/L is required, if matrix spike recovery is not within 80-120%. The method of standard additions (see Method 7000A, section 8.7, SW-846, 3rd. Ed. July 1992) is required.

10.7 Leaded gasoline or Reference Standard with a known concentration of organolead must be used as the spiking solution for all sample types, at 2-3 times the level of actual sample concentration. Spike recoveries should be within 80-120%.

11. Method Performance

11.1 Method Detection Limit: The Method Detection Limit studies were carried out using eleven replicates, each of water, soil and oil samples spiked with Reference standard NIST, SRM 2715 (lead in Reference fuel).

The following table summarizes the data:

	WATER(: g/L)	SOIL(: g/Kg)	OIL(: g/Kg)
Amt spiked	13.5	39.2	105
Mean	13.0	37.2	105
% Recovery	96.6	94.9	100
standard deviation	0.4334	3.365	5.55
MDL (sd x 2.76)	2.00	15.0	15.0
Lowest Standard	5.00	20.0	20.0
QL(Lowest Std x DF)	5.00	50.0	125

11.2 The instrument detection limit (IDL) was determined by the analysis of eleven replicates of blanks and standards. The IDL was based on 2.76 times the standard deviation which was 1.02 : g/L.

11.3 The following soil samples were spiked with organolead and a high level of inorganic lead compounds, to determine the interference of inorganic lead. Two sets of three replicates of clean soil samples were saturated with water. Each set was spiked with 2.0 ml of 0.54 mg/L of organolead standard prepared in xylene. The first set was spiked with 2.0 ml of 10g/L of lead prepared from lead nitrate in deionized water, 2nd set was spiked with 2.0 ml of 5.0 g/L of Pb prepared from lead chloride, and mixed with anhydrous sulfate. Two blank replicates of each set were prepared as the sample preparation without organolead standard spike.

	Set I		Set II	
	$Pb(NO_3)_2$	Organolead	$PbCl_2$	Organolead
Blank(: g/Kg)	<10.0	<10.0	<10.0	<10.0
Spike Added	500mg/Kg	43.2 : g/Kg	298mg/Kg	43.2 : g/Kg
Mean Recovered	<10.0 : g/Kg	44.0 : g/Kg	<10.0 : g/Kg	44.6 : g/Kg
Mean % Recovery	0.0	102	0.0	103
Mean % RSD		7.50		3.05

The results show that the recovery of $Pb(NO_3)_2$ or $PbCl_2$ was negligible, which indicated that there was no inorganic Pb extracted with this method.

12. References

12.1 Du Pont Petroleum Laboratory, Petroleum Laboratory Method M-111-74.

12.2 American National Standard Institute/American Society for Testing and Materials (ANSI/ASTM), ASTM D3237-79, "Standard Test Method for Lead in gasoline by Atomic Absorption Spectrometry."

12.3 Varian, Analytical Methods for Graphite Tube Atomizers

12.4 Test Methods for Evaluating Solid Waste Method 7000A, SW-846, 3rd. Ed. U. S. Environmental Protection Agency, July 1992.